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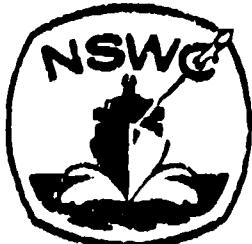
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Migration of Explosives in Soil

BY ELEONORE G. KAYSER, NICHOLAS E. BURLINSON
RESEARCH AND TECHNOLOGY DEPARTMENT

6 DECEMBER 1982

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20. (Cont.)

TNT was not observed in any of the TNT water samples either by gc/ee or hplc. None of the typical TNT biodegradation or oxidation products were observed. Analysis of the TNT soil extracts revealed the presence of TNT and two biotransformation products of TNT.

Trace amounts of picric acid were detected in the tetryl water samples which also contained nonvolatile, highly polar products.

Analysis of the RDX water samples revealed RDX and the impurity HMX in the leachate. The RDX soil extracts contained RDX, HMX, volatile decomposition products as well as polar nonvolatile decomposition products.

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FOREWORD

This report contains the analytical results of 121 water samples and 24 soil samples obtained from a Battelle Columbus Laboratories ^{14}C lysimeter study of TNT, RDX, and tetryl. The study was funded by the U.S. Army Medical Bioengineering R & D Laboratory (USAMBRDL), Fort Detrick, Maryland, to assess the environmental fate of these three explosives in various soils. Forty-six of the 121 water samples received had ^{14}C activity greater than 100 dpm/ml and were further analyzed by gc/ec, hplc, and tlc methods.

TNT was not observed in any of the TNT water samples either by gc/ec or hplc. None of the typical TNT biodegradation or oxidation products were observed by hplc in any of the TNT water samples. One of the highest ^{14}C activity TNT water samples in the Princeton-TNT sample revealed only highly polar, nonvolatile products, none of which could be separated or identified. Analysis of the TNT soil extracts revealed the presence of two biotransformation products of TNT, the 4-amino-2,6-dinitrotoluene and the 2-amino-4,6-dinitrotoluene.

Only three tetryl water samples had sufficient ^{14}C activity to warrant analysis. Tetryl could not be detected in these by hplc analysis but trace amounts of picric acid were confirmed. Tlc analysis of one of the tetryl water samples (Bennington #6/22) revealed only nonvolatile, highly polar products which could not be separated or identified.

Analysis of the Princeton-RDX water samples revealed increasing concentrations of RDX in the leachate. HMX, the impurity in RDX was present to the extent of ~10% of the RDX amount in each water sample. The Genesee-RDX water samples also had RDX but only 1/10 of the level of that of the Princeton-RDX water samples. The Bennington and Brookston RDX water samples contained virtually no RDX. Tlc and ^{14}C analysis of the residue from evaporation of the Princeton-RDX #8/22 water sample revealed RDX, HMX, ^{14}C labeled volatile decomposition products as well as ^{14}C labeled polar nonvolatile decomposition products.

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INTRODUCTION

This report contains the analytical results of 121 water samples and 24 soil samples obtained from a Battelle Columbus Laboratories ^{14}C lysimeter study of TNT, RDX, and tetryl. The study was funded by the U.S. Army Medical Bioengineering R & D Laboratory (USAMBRDL), Fort Detrick, Maryland, to assess the environmental fate of these three explosives in various soils.

USAMBRDL asked the Naval Surface Weapons Center (NSWC), White Oak to analyze the water and soil samples from the Battelle Study for (1) ^{14}C activity, (2) TNT, RDX, and tetryl content, and (3) any transformation or degradation products of these explosives. In January 1979, NSWC received a shipment of 121 water samples and 24 6-inch sections of the soil samples. The soil samples received included the complete set of 16 sections of TNT soil samples, 4 Princeton RDX soil sections, and 4 Genesee RDX soil sections. However, none of the tetryl soil samples were included in the ^{14}C sample shipment sent to NSWC.

OBJECTIVES

The objectives of the NSWC analyses were (1) to determine the ^{14}C activity of each water sample and compare the results with those obtained earlier by Battelle; (2) to quantitatively analyze for TNT, tetryl, or RDX in the water samples where ^{14}C activity was greater than 100 dpm per mL (0.5 $\mu\text{g/mL}$); (3) to analyze for transformation products in the water samples; (4) to check for volatile products; (5) to analyze each soil section for total ^{14}C activity and for total explosive content; and finally (6) to analyze for any transformation products in the soil samples.

SAMPLE HISTORY

At Battelle, the explosives were mixed with four "standard soils" and then irrigated with water for 6 months. The explosives' propensity for downward movement and for transformation in the particular soils columns (lysimeters) was to be determined. To aid this analytical study, each explosive was ring-labeled with radioactive carbon-14. The four soils used in this study were Princeton, Genesee, Brookston, and Bennington.

The soils were packed into steel columns, 24 inches long and 2 inches in diameter. The top 3 inches of soil were removed from each column, and 4 grams of one of the ^{14}C labeled explosives were uniformly mixed with this portion of the soil. The mixtures were then added back to the top of the steel columns (lysimeters).

The ^{14}C activity of each explosive contained in the soil was such that 200 disintegrations per minute (dpm) corresponded to 1 microgram of explosive. Each column therefore contained 8.0×10^8 dpm of ^{14}C activity at the start of the lysimeter test.

Twelve columns (3 explosives with 4 different soils) were then irrigated with distilled water for 6 months at Battelle. Every 2 weeks, a water sample was taken from the bottom of each column. After 6 months, each column was cut into four 6-inch sections for analysis.

EXPERIMENTAL

ANALYTICAL METHODS

Liquid Scintillation Counting of both water and soil samples was done with a Searle Co. Scintillation Counter (model-Unilux 2-A). The sample disperser was Eastman CAB-OSIL M-5 Scintillation Grade, and the solvent was Aquasol Universal Cocktail.

Gas Chromatography (gc) was used to assay for TNT and tetryl in the water samples. An HP-5700 gas chromatograph with electron capture (ec) detection was used. The water samples were extracted with benzene 1:1 (2, 4, 6 trinitro-1,3-dimethoxybenzene was used as an internal standard). By this procedure concentrations down to 0.3 $\mu\text{g/L}$ can be observed without concentrating the extract.

High Performance Liquid Chromatography (hplc) was also used to assay both water and soil samples for TNT, tetryl, and RDX. A Waters Model ALC 202/440 isocratic hplc with an M-6000A pump and 254 nm detection was used. The analytical column was a reverse-phase Whatman 10 μm Partisil ODS-2 using methanol/water (40/60) as solvent at a flow rate of 2 ml/min. By this analytical method, concentrations down to 50 $\mu\text{g/L}$ could be observed using 100 μL injections at the most sensitive setting of the Waters 440 detector (.005 AUFS).

Thin Layer Chromatography (tic) was also used to separate and quantitate the explosives and their transformation products in both water and soil samples. Merck Silica Gel HF-254 coated on glass plates, was used as the absorbent; and benzene, methanol, and a mixture of benzene/ether/ethanol (50:30:20) were the three solvent systems used. UV-visible spots on the tic plate were scraped off and their ^{14}C activities determined directly by scintillation counting.

Soil Extraction Procedure

1. Each soil segment was scraped out from the metal casing.
2. Ten to twenty grams of the soil were dried overnight at 70°C, then reweighed to determine the water content in each segment.
3. Each ^{14}C -TNT soil segment was extracted with 800 mL benzene. The soil was stirred in the extracting solvent for 20 minutes, filtered, and extracted a second time with 800 mL of fresh benzene and the extracts combined. The above extracted soil was then re-extracted in a like fashion a third and fourth time with acetone (500 mL each) and filtered. The acetone extracts were combined.
4. The benzene and acetone extracts were then reduced in volume at room temperature to the point where all the extracted products remained in solution. These solutions or dilutions thereof were used in the liquid scintillation counter, hplc, or tlc to identify and quantitate the ^{14}C -TNT and other transformation products.
5. The residual ^{14}C activity left on the extracted soil was determined by liquid scintillation counting techniques after drying the soils at 50°C overnight.
6. The same procedures were used for the ^{14}C RDX soil samples, however, due to the relative insolubility of RDX in benzene, only acetone was used as the extraction solvent (total acetone = 800 mL).

Data on Standard Compounds. Table 1 shows the hplc and tlc data of the explosive compounds and some of their transformation products.

ANALYTICAL RESULTS

ANALYSIS OF WATER SAMPLES

Analysis of ^{14}C Activity in Water Samples

All 121 water samples received from Battelle were analyzed for ^{14}C activity. The counts in Tables 2, 3, and 4 show a close correlation with those reported by Battelle. Based on Battelle's specific activity figures, a ^{14}C activity of 100 dpm/mL corresponds to a concentration of 0.5 mg/L of the explosive and/or its transformation products in the water samples. Forty-six water samples had ^{14}C activity greater than 100 dpm/mL and were further analyzed by gc, hplc, and tlc.

Gas Chromatographic Analysis of Water Samples

1. TNT Water Samples. TNT was not found by the gc/ec method in any of the TNT water samples. Concentrations down to 0.5 ug/L can typically be detected by this method without concentrating the 1:1 benzene extract.

TABLE 1. HPLC AND TLC DATA OF EXPLOSIVE COMPOUNDS

<u>Compound</u>	<u>hplc Retention Times (min.)</u>	<u>hplc Relative Response Factor (254 nm)</u>	<u>tlc RF (benzene)</u>
TNT	13.3	0.84	0.83
PiH	6.8	1.00	0.80
4A26DNT	16.8	0.43	0.28
2A46DNT	18.7	0.80	0.28
2,6DA4NT	3.0	0.97	0.03
2,4DA6NT	3.4	0.48	0.03
RDX	5.4	0.33	0.32
HMX	2.8	0.32	0.17
Cyclohexanone	5.2	15.80	----
Tetryl	13.0	0.65	0.7
Picric Acid	1.0	1.40	0.0

TABLE 2. ^{14}C ACTIVITY OF TNT WATER SAMPLES^(a)

<u>Samples</u>	<u>Battelle Data (dpm)</u>	<u>NSWC Data (dpm)^(b)</u>
Bennington-TNT	all <500	all <500
Brookston-TNT	all <500	all <500
Genesee-TNT		
4/20/77 ^(c)	684	(d)
6/15	597	(d)
6/29	610	(d)
7/13	1,358	(d)
7/27	1,097	699
8/10	1,944	1,367
8/24	2,220	849
Princeton-TNT		
4/20/77	825	(d)
5/4	5,130	5,250
5/18	16,753	17,174
6/1	18,651	18,543
6/15	15,662	15,076
7/13	13,451	13,261
7/27	16,734	14,072
8/10	11,676	11,340
8/24	10,627	10,660

(a) Sample size = 5 mL

(b) Error of NSWC ^{14}C measurement = \pm 200 dpm

(c) Sample number = date when sample was taken by Battelle

(d) Samples filtered and solid material checked for ^{14}C activity--neither filtrate or solids showed activity above 500 dpm

TABLE 3. ^{14}C ACTIVITY OF TETRYL WATER SAMPLES^(a)

<u>Samples</u>	<u>Battelle Data(dpm)</u>	<u>NSWC Data.(cpm)^(b)</u>
Bennington-tetryl 6/22/77(c)	1,809	1,448
Brookston-tetryl 6/22/77	3,752	3,065
Genesee-tetryl 4/27/77 5/25 6/22 7/6 7/20 8/3 8/17	1,582 1,215 1,472 1,392 1,160 2,190 1,335	(d) 529 (d) (d) (d) (d) (d)
Princeton-tetryl	all <500	all <500

- (a) Sample size = 5 mL
- (b) Error of NSWC ^{14}C measurement = \pm 200 dpm
- (c) Sample number = date when sample was taken by Battelle
- (d) Samples filtered and solid material checked for ^{14}C activity--neither filtrate or solids showed activity above 500 dpm.

TABLE 4. ^{14}C ACTIVITY OF RDX WATER SAMPLES^(a)

<u>Samples</u>	<u>Battelle Data(dpm)</u>	<u>NSWC Data(dpm)^(b)</u>
Bennington-RDX		
6/27/77 ^(c)	5,220	3,898
6/11/77	543	<500
Brookston-RDX	all <500	all <500
Genesee-RDX		
4/4/77	885	742
4/18	1,815	2,700
5/2	2,504	2,243
5/16	9,125	10,549
5/30	5,279	4,744
6/13	36,056	34,262
6/27	34,180	42,252
7/11	6,994	6,975
8/8	17,030	16,057
8/22	24,566	22,121
Princeton-RDX		
4/18/77	676	794
5/2	4,490	4,317
5/16	11,317	12,807
5/30	22,783	23,202
6/27	65,557	68,795
7/11	94,382	102,609
7/25	104,465	121,019
8/8	124,913	129,294
8/22	134,999	138,281

(a) Sample size = 5 mL

(b) Error of NSWC ^{14}C measurement = \pm 200 dpm

(c) Sample number = date when sample was taken by Battelle

2. Tetryl Water Samples. Tetryl was not found in any of three tetryl water samples by the gc/ec method. The limit of concentration of tetryl is less than 0.3 $\mu\text{g}/\text{L}$ in these samples extracted with benzene (1:1). Details of the gc/ec analytical procedure are discussed in the section on analytical methods.

3. RDX Water Samples. These samples were not analyzed by gc/ec but by hplc and tlc methods (see below).

Liquid Chromatographic (hplc) Analysis of Water Samples

1. TNT Water Samples. Those samples with ^{14}C activities greater than 100 dpm/mL, were analyzed directly (i.e., no extraction or filtering) by reverse-phase liquid chromatography (details above). TNT was not found by this method where concentrations down to 50 $\mu\text{g}/\text{mL}$ are observable using 100 μL injections. Also, none of the known TNT biotransformation products¹ (e.g., 4-amino-2,6-dinitrotoluene, 2-amino-4,6-dinitrotoluene or the diamino derivatives of TNT) were observed by this method. Nor were other commonly known TNT degradation products^{2,3} found (i.e., trinitrobenzene, trinitrobenzyl alcohol, trinitrobenzaldehyde, or trinitrobenzoic acid). The azoxytoluenes, also identified by NSWC⁴ during an earlier TNT biodegradation investigations were not found in these water samples.

2. Tetryl Water Sample. Of the three samples which had sufficient ^{14}C activity to warrant analysis (Table 3), none showed any LC absorption corresponding to tetryl. However, a peak corresponding to picric acid, a known⁵ hydrolysis product of tetryl, was observed by LC in each of the three tetryl water samples. These analyses show that picric acid comprised 14% of the total ^{14}C activity in the Bennington 6/22 tetryl sample, 5% in the Brookston 6/22 tetryl sample, and 10% in the Genesee 5/11 tetryl sample. Quantitation of picric acid was verified by tlc by removing the spot corresponding to picric acid and counting its ^{14}C content.

¹Hoffsommer, J. C., et al., Biodegradability of TNT: a Three Year Pilot Plant Study, NSWC/WOL/TR 77-136, 1978.

²Burlinson, N. E., et al., "Photochemistry of TNT and Related Nitroaromatics, Part III," Final Report submitted to USAMBRDL, Fort Detrick, MD, 1979.

³Burlinson, N. E., "Photodecomposition and Biotransformation of TNT in River Water," Final Report submitted to USAMBRDL, Fort Detrick, MD, 1979.

⁴Hoffsommer, J. C., Glover, D. J., Heckley, R. J., and Won, W. D., "Metabolic Disposition of TNT," Appl. Microbiol. 27, 513-16 (1974).

⁵Hoffsommer, J. C., and Rosen, J. M., "Hydrolysis of Explosives in Sea Water," Bull. Envir. Contamination and Toxicology, 10, 1, 1973 p. 75.

3. RDX Water Samples. Those samples with sufficient ^{14}C activity (Table 4) were analyzed by hplc using the same method reported above for TNT and tetryl. The hplc analysis results are in Table 5 with tlc quantitative analysis results for RDX and an hplc analysis result for HMX. HMX is the expected impurity in production grade RDX and is usually present at a concentration of 8-13%. The final column in Table 5 represents the total ^{14}C activity in each water sample converted to RDX in $\mu\text{g/mL}$. The data show that the actual concentration of RDX in the Princeton and Genesee water samples is ~28% and ~8% respectively of the ^{14}C activity. Note that the ^{14}C activity of the Princeton RDX samples dated 6/27 to 8/22 is higher than the solubility of RDX in water ($45 \mu\text{g/mL}$ at 25°C), indicating that RDX decomposed in the soil and the products were flushed out in the leachate.

Analysis of Water Samples for Volatile Decomposition Products

1. TNT. A small quantity of Princeton/TNT water sample #5/18, with 17,174 counts which showed no TNT present by gc and hplc, was evaporated to dryness at room temperature, then recounted. The counts remained the same, indicating an absence of volatile decomposition products. This sample was also extracted with benzene (1:1) and the benzene layer counted for ^{14}C activity. A level of 100 dpm/5 mL was observed, indicating that the TNT decomposition products were quite polar and water-soluble.

2. Tetryl. The same treatment was applied to Bennington/tetryl water sample #6/22 containing 1,448 counts. The same results on volatility and extraction were observed as with the TNT water sample, indicating polar/water-soluble decomposition products.

3. RDX. The same treatment was applied to Princeton RDX water sample #8/22 with 138,281 counts, and it revealed 40% volatile decomposition products with 25% of the activity due to benzene-soluble material (mostly RDX).

Analysis of Solid Residues From Water Samples By TLC

Using the same three most active water samples (Princeton-TNT 5/18, Princeton-RDX 8/22, and Bennington-tetryl 6/22), thin layer chromatographic analyses of the solid residues from each of these water samples was conducted. It was hoped that this method would isolate some decomposition products. A 5.0 mL aliquot of the water sample was taken to dryness at room temperature, then redissolved in 0.5 mL of water and the entire amount spotted on a tlc plate. Standards of the known biotransformation and hydrolysis products for each explosive were also run on the same plate as the unknown residues. Then areas of the plate were removed directly into the scintillation vial for ^{14}C counting.

Table 6 contains the tlc analysis data of the Princeton-TNT 5/18 sample which showed no evidence of TNT or its known biotransformation products. No evidence of any other benzene chromatographable polynitroaromatic compounds associated with the photochemical, thermal, or alkaline decomposition of TNT (i.e., PiCHO , PiCH_2OH , $\text{PiCH}_2\text{CH}_2\text{Pi}$, PiH , etc.) was found.

TABLE 5. ANALYSIS OF RDX AND HMX IN WATER SAMPLES

<u>Sample Number (date)</u>	<u>RDX by tlc ($\mu\text{g}/\text{mL}$)</u>	<u>RDX by hplc ($\mu\text{g}/\text{mL}$)</u>	<u>HMX by hplc ($\mu\text{g}/\text{mL}$)</u>	<u>RDX by ^{14}C Activity ($\mu\text{g}/\text{mL}$)^(a)</u>
Princeton-RDX				
5/22/77	1.2	1.4		4.3
5/16	3.4	4.0	0.36	12.8
5/30	6.0	6.0	0.60	23.2
6/27	17.8	18.0	1.80	68.8
7/11	26.6	27.0	2.70	102.6
7/25	31.4	34.0	3.40	121.0
8/22	36.0	40.0	3.60	138.0
Genesee-RDX				
4/18/77	0.28	0.14		2.7
5/2	0.22	0.14		2.2
5/16	1.06	0.52	0.04	10.5
5/30	0.48	0.40	0.04	4.7
6/13	3.40	4.00	0.36	34.3
6/27	4.20	4.20	0.46	42.2
7/11	0.70	0.58	0.06	7.0
8/8	0.16	1.62	0.14	16.0
8/22	2.20	2.54	0.24	22.1
Bennington-RDX				
6/27/77	0.78	0.68	0.06	3.9

(a) Theoretical RDX based on ^{14}C activity in water sample, assuming no decomposition.

TABLE 6. ANALYSIS OF TNT, TNT-BIOTRANSFORMATION STANDARDS
AND PRINCETON-TNT 5/18 BY TLC

TNT and TNT Biotransformation Standards

	<u>Rf(benzene)</u>	<u>Rf(Magic)</u>	<u>Rf(MeOH)</u>
TNT	0.78	1.00	1.0
2NH ₂ -4,6-DNT	0.20	1.00	1.0
4NH ₂ -2,6-DNT	0.23	1.00	1.0
2,4NH ₂ -6-NT	0.03	0.94	1.0
2,6NH ₂ -4-NT	0.03	0.96	1.0

Princeton-TNT 5/18

<u>Rf(benzene)</u>	<u>%¹⁴C</u>	<u>Rf(Magic)^(a)</u>	<u>%¹⁴C</u>	<u>Rf(MeOH)</u>	<u>%¹⁴C</u>
0.61-0.79	0	0.58-0.91	3	0.83-0.95 ^(b)	59
0.44-0.61	0	0.07-0.58 ^(b)	65	0.07-0.83 ^(b)	13
0.26-0.44	0	0.0-0.07 ^(b)	30	0.07-0.07 ^(b)	11
0.07-0.26	0				
0.0-0.07	98%				

(a) Magic Solvent = benzene/ether/ethanol, 50:30:20

(b) No distinct spots-tailing occurring

Table 7 contains the analysis data of the Princeton-RDX 5/12 sample which showed the presence of HMX, RDX, and 50% ^{14}C volatile material. Other known hydrolysis or alkaline degradation products such as formic acid or formaldehyde could not be assayed for by tlc. However, in separate experiments on the "Princeton-RDX 8/22" water sample, tests for formaldehyde and formic acid were carried out. The chromatropic acid test for formaldehyde was negative, but this test is misleading if NO_2^- and NO_3^- are present. Therefore, the "nitrobenzene method" of Hoffsommer and Glover was used to determine NO_2^- and NO_3^- concentrations.⁶ Results of the test showed a nitrate concentration of $2.31 \times 10^{-3}\text{M}$ and a nitrite concentration of $5.8 \times 10^{-4}\text{M}$.

The combined $\text{NO}_2^- + \text{NO}_3^-$ concentration found is approximately 50% more than the value expected from the decomposition of the theoretical RDX value of 138 $\mu\text{g/mL}$ (Table 5) less the actual 36 $\mu\text{g/mL}$ RDX. This result suggests several possibilities: (1) RDX could be decomposing on the soil, releasing NO_2^- and/or NO_3^- which is flushed out of the lysimeter with water but leaving the ^{14}C tagged species absorbed on the soil; or (2) a background concentration of $\text{NO}_2^-/\text{NO}_3^-$ in the soil would give high readings; or (3) more than three of the six RDX nitrogen atoms are ending up as NO_2^- and/or NO_3^- .

Table 8 contains the tlc analysis data of the Bennington-tetryl 6/22 sample which indicates the presence of picric acid but no tetryl. Therefore a combined tlc/hplc analysis was carried out on the only three water samples (Bennington-tetryl 6/22, Brookston-tetryl 6/22, and Genesee tetryl 5/11) to be analyzed. The concentration of picric acid in the above samples was determined by measurement of ^{14}C activity in isolated tlc spots and by peak area in hplc. These analyses showed that picric acid comprised 14% of the total ^{14}C activity in the Bennington 6/22 sample, 5% in the Brookston sample, and 10% in the Genesee sample.

ANALYSIS OF SOIL SAMPLES

All reported quantities and concentrations are based on ^{14}C analysis of extracts or tlc spots (see Experimental Section). Also, based on Battelle's ^{14}C activity data, 1 microgram of explosive corresponds to 200 dpm and 4.00 g of total explosive were initially added to each soil column.⁷

⁶Glover, D. J., and Hoffsommer, J. C., "Gas Chromatographic Analysis of Nitrate and Nitrite Ions in Microgram Quantities by Conversion to Nitrobenzeno," Journal of Chromatography, 94, 1974, pp. 334-337.

⁷Hale, V. Q., Stamford, T. B., and Taft, L. G., "Evaluation of the Environmental Fate of Munition Compounds in Soil," Final Report from Battelle Columbus Labs. submitted to USAMBRDL, Fort Detrick, MD.

TABLE 7. ANALYSIS OF RDX/HMX, RDX DEGRADATION PRODUCTS
AND PRINCETON-RDX 8/22 BY TLCRDX/HMX Standards

	<u>Rf(benzene)</u>	<u>Rf(Magic)</u>
RDX	0.11	1.00
HMX	0.03	0.94
Formic Acid	0.00	0.00
Formamide	0.00	0.47

Princeton-RDX 8/22^(a)

<u>Rf(benzene)</u>	<u>%¹⁴C</u>	<u>Rf(Magic)</u> (b)	<u>%¹⁴C</u>	<u>Rf(MeOH)</u>	<u>%¹⁴C</u>
0.68-1.0	0	0.77-1.0	33	0.77-1.0	31
0.30-0.68	0	0.07-0.77	12	0.07-0.77	13
0.08-0.30	26	0.0-0.07	7	0.0-0.07	5.3
0.0-0.08	23				

(a) 50% of ¹⁴C activity due to volatile material

(b) Magic Solvent = benzene/ether/ethanol, 50:30:20

TABLE 8. ANALYSIS OF TETRYL, PICRIC ACID, AND THE BENNINGTON-TETRYL 6/22 SAMPLE BY TLC

Tetryl/Picric Acid Standards

	<u>Rf(benzene)</u>	<u>Rf(Magic)</u>
tetryl	0.7	1.0
Picric Acid	0.0-0.17	0.45

Bennington-Tetryl 6/22

<u>Rf(benzene)</u>	<u>%¹⁴C</u>	<u>Rf(Magic)</u>	<u>%¹⁴C</u>
0.79-1.0	0	0.92-1.0	80
0.62-0.79	0	0.07-0.92	14(picric)
0.44-0.62	0	0.0-0.07	6
0.26-0.44	0		
0.07-0.26	52		
0.0-0.07	48 (picric)		

The soil samples analyzed were:

Princeton-TNT
Genesee-TNT
Brookston-TNT
Bennington-TNT
Princeton-RDX
Genesee-RDX

Visual observations of the different soil porosities coincided with the observations described in Battelle's report. It should be noted that Battelle had removed for its analysis 16% of each soil column (bottom 1 inch of each 6 inch section).

Listed below are the segments of the soil columns used for the NSWC analysis:

Segment 1--0-5 inches soil
Segment 2--7-11 inches
Segment 3--13-17 inches
Segment 4--19-23 inches

The following analytical results are recorded by segments of each soil column and reflect ^{14}C , tlc, and hplc analyses of the extracts of those segments. The quantities of explosive, and explosive degradation products found in each segment of soil are tabulated in Tables 9 through 14. The amounts were determined by counting the ^{14}C activity in tlc spots of the soil extracts (benzene and acetone extracts combined). When looking at the theoretical material balance (based on ^{14}C count), it must be remembered that 16% of the soil from each section is missing (used by Battelle for analysis). Also that the total amount of activity found in the water samples from each column is negligible (0.1%) compared to the original total ^{14}C activity (800,000,000 dpm) on each column.

TABLE 9. PRINCETON TNT SOIL SAMPLE SUMMARY

Column Segments	Materials	TLC Data (grams)	HPLC Data (grams)	Total TLC Data (grams)
segment 1 0-5"	TNT	1.550	1.78	
	2A + 4A	0.057		
	tlc origin	0.106		
	unextractable	0.329		
segment 2 7-11"	TNT	0.140	0.107	
	2A + 4A	0.412	0.45	
	tlc origin	0.604		
	unextractable	0.229		
segment 3 13-17"	TNT	0.0007		
	2A + 4A	0.003		
	tlc origin	0.011		
	unextractable	0.056		
segment 4 19-23"	TNT	6.0×10^{-6}		
	2A + 4A	6.2×10^{-5}		
	tlc origin	3.1×10^{-4}		
	unextractable	0.004		
segments 1+2+3+4	TNT			1.69
	2A + 4A			0.47
	tlc origin			0.72
	unextractable			0.59

Total weight = 3.47 g = 87% theoretical material balance

TABLE 10. GENESEE TNT SOIL SAMPLE SUMMARY

Column Segments	Materials	TLC Data (grams)	HPLC Data (grams)	Total TLC Data (grams)
segment 1 0-5"	TNT	2.122	2.20	
	2A + 4A	0.269		
	tlc origin	0.043		
	unextractable	1.300		
segment 2 7-11"	TNT	0.018	0.015	
	2A + 4A	0.008	0.009	
	tlc origin	0.009		
	unextractable	0.137		
segment 3 13-17"	TNT	0.0001	0.0001	
	2A + 4A	0.0002	0.00014	
	tlc origin	0.0002		
	unextractable	0.018		
segment 4 19-23"	TNT	<1.0 μ g	0.04 μ g	
	2A + 4A	2.5 μ g	4.0 μ g	
	tlc origin	20.0 μ g		
	unextractable	0.0027		
segments 1+2+3+4				2.14
	TNT			0.277
	2A + 4A			0.052
	tlc origin			
	unextractable			1.46

Total weight = 3.93 g = 98% theoretical material balance

TABLE 11. BROOKSTON TNT SOIL SAMPLE SUMMARY

Column Segments	Materials	TLC Data (grams)	HPLC Data (grams)	Total TLC Data (grams)
segment 1 0-5"	TNT	2.94	2.93	
	2A + 4A	0.070		
	tlc origin	0.077		
	unextractable	0.756		
segment 2 7-11"	TNT	0.0001	0.00013	
	2A + 4A	0.0006		
	tlc origin	0.0004		
	unextractable	0.030		
segment 3 13-17"	not analyzed			
segment 4 19-23"	not analyzed			
segments 1+2	TNT			2.94
	2A + 4A			0.07
	tlc origin			0.08
	unextractable			0.79

Total weight in segments 1 and 2 = 3.88 g = 97% theoretical material balance

TABLE 12. BENNINGTON TNT SOIL SAMPLE SUMMARY

Column Segments	Materials	TLC Data (grams)	HPLC Data (grams)	Total TLC Data (grams)
segment 1 0-5"	TNT	2.774	2.82	
	2A + 4A	0.168		
	tlc origin	0.232		
	unextractable	0.548		
segment 2 7-11"	TNT	0.0001	0.0009	
	2A + 4A	0.001	0.0006	
	tlc origin	0.0004		
	unextractable	0.008		
segment 3 13-17"	TNT	3 μ g		
	2A + 4A	14 μ g		
	tlc origina	11 μ g		
	unextractable	283 μ g		
segment 4 19-23"	not analyzed			
segments 1+2+3	TNT		2.774	
	2A + 4A		0.169	
	tlc origin		0.232	
	unextractable		0.556	

Total weight in segments 1, 2, and 3 = 3.731 g = 93% theoretical material balance

TABLE 13. PRINCETON RDX SOIL SAMPLE SUMMARY

Column Segments	Materials	TLC Data (grams)	HPLC Data (grams)	Total TLC Data (grams)
segment 1 0-5"	RDX	1.513	1.560	
	HMX	0.210	0.185	
	tlc origin	0.162		
	unextractable	0.409		
	volatile	0.101		
segment 2 7-11"	RDX	0.638	0.699	
	HMX	0.113	0.063	
	tlc origin	0.094		
	unextractable	0.059		
	volatile	0.040		
segment 3 13-17"	RDX	0.014		
	HMX	0.012		
	tlc origin	0.006		
	unextractable	0.004		
	volatile	0.001		
segment 4 19-23"	RDX	0.0044		
	HMX	0.0024		
	tlc origin	0.0016		
	unextractable	0.003		
	volatile	0.011		
segments 1+2+3+4				2.169
	RDX			0.337
	HMX			0.264
	tlc origin			0.475
	unextractable			0.153

Total weight = 3.398 g = 85% theoretical material balance

TABLE 14. GENESEE RDX SOIL SAMPLE SUMMARY

Column Segments	Materials	TLC Data (grams)	HPLC Data (grams)	Total TLC Data (grams)
segment 1 0-5"	RDX	1.904	2.129	
	HMX	0.386	0.252	
	tlc origin	0.342		
	unextractable	0.571		
	volatile	--		
segment 2 7-11"	RDX	0.036	0.034	
	HMX	0.006	0.006	
	tlc origin	0.013		
	unextractable	0.010		
	volatile	0.003		
segmenc 3 13-17"	RDX	0.003	0.0024	
	HMX	0.0004	0.0004	
	tlc origin	0.001		
	unextractable	0.005		
	volatile	0.0008		
segment 4 19-23"	RDX	0.003		
	HMX	0.0003		
	tlc origin	0.001		
	unextractable	0.004		
	volatile	0.0007		
segments 1+2+3+4	RDX			1.946
	HMX			0.393
	tlc origin			0.3576
	unextractable			0.590
	volatile			0.004

Total weight = 3.290 g = 82% theoretical material balance

SUMMARY

1. Forty-six of the 121 water samples received had ^{14}C activity greater than 100 dpm/mL and were further analyzed by gc/ec, hplc, and tlc methods.
2. TNT was not observed in any of the TNT water samples either by gc/ec (<0.3 $\mu\text{g/L}$) or by hplc (<50 $\mu\text{g/L}$).
3. None of the typical biodegradation or oxidation products of TNT were observed by hplc in any of the TNT water samples.
4. One of the highest ^{14}C activity TNT water samples was Princeton-TNT #5/18 with 17,174 dpm/5 mL which is equivalent to 86 $\mu\text{g}/5 \text{ mL}$; this activity would correspond to 17 ppm TNT. However tlc analysis of this sample revealed only highly polar, nonvolatile products, none of which could be separated or identified.
5. Analysis of the TNT soil extracts revealed the presence of two biotransformation products of TNT, the 4-amino-2,6-dinitrotoluene and the 2-amino-4,6-dinitrotoluene. The Princeton-TNT soil sample contained as much as 6% of each aminodinitrotoluene (ADNT) but the Genesee-TNT soil contained only 0.1% of each of the ADNTs. The Bennington-TNT soil had only 0.02% each of the ADNTs while the Brookston-TNT soil showed only 0.01% of the 4A26DNT isomer.
6. Only three tetryl water samples had sufficient ^{14}C activity to warrant analysis. Tetryl could not be detected in these by hplc analysis (lower limit 0.05 mg/L) but trace amounts of picric acid (~0.15 mg/L) were confirmed.
7. Tlc analysis of one of the tetryl water samples (Bennington #6/22) revealed only nonvolatile, highly polar products which could not be separated or identified.
8. Analysis of the Princeton-RDX water samples revealed increasing concentrations of RDX in the leachate (from 1.4 mg/L in the 5/2 sample to 40.0 mg/L in the 8.22 sample). HMX, the impurity in RDX was present to the extent of ~10% of the RDX amount in each water sample. The Genesee-RDX water samples also had RDX but only at 1/10 the level of that of the Princeton-RDX water samples. The Bennington and Brookston RDX water samples contained virtually no RDX.
9. Tlc and ^{14}C analysis of the residue from evaporation of the Princeton-RDX #8/22 water sample revealed the following concentrations: 40 mg/L RDX, 4 mg/L HMX, 60 mg/L ^{14}C labeled volatile decomposition products and approximately 30 mg/L of other ^{14}C labeled polar nonvolatile decomposition products.

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NOMENCLATURE

dpm = disintegrations per minute

gc/ec = Gas Chromatography/Electron Capture

HMX = 1,3,5,7-tetranitro - 1,3,5,7-tetraazacyclooctane

hplc = High Pressure Liquid Chromatography

NO₂⁻ = Nitrite

NO₃⁻ = Nitrate

PiCHO = 2,4,6-trinitrobenzaldehyde

PiCH₂CH₂Pi = hexanitrobibenzyl

PiCH₂OH = 2,4,6-trinitrobenzyl alcohol

PiH = 1,3,5-trinitrobenzene

RDX = 1,3,5-trinitro-1,3,5-triazacyclohexane,
cyclo-1,3,5-trimethylene-2,4,6-trinitramine, cyclonite

tetryl = N,2,4,6-tetranitro-N-methylaniline

tlc = Thin Layer Chromatography

TNT = 2,4,6-trinitrotoluene

2A = 2A46DNT = 2NH₂46DNT = 2-amino-4,6-dinitrotoluene

2,4NH₂-6-NT = 2,4DA6NT = 2,4-diamino-6-nitrotoluene

2,6NH₂-4NT = 26DA4NT = 2,6-diamino-4-nitrotoluene

4A = 4A26DNT = 4NH₂-2,6-DNT = 4-amino-2,6-dinitrotoluene

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